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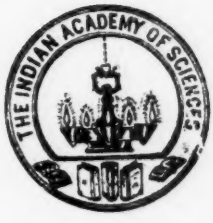

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X-RAY STUDY OF FIBROUS QUARTZ

By Sir C. V. Raman and A. Jayaraman
(*Memoir No. 57 from the Raman Research Institute, Bangalore*)

Received September 16, 1954

1. Introduction

Mineralogists designate a mineral as fibrous when it consists of visibly distinct rods or threads, irrespective of whether these are separable or not from each other. Many gradations between a coarsely columnar and a finely fibrous structure are to be observed, the finely fibrous materials often exhibiting a silky lustre. In his *Handbuch der Mineralogie*, Hintze[1] reports that secondary quartz often appears as pseudomorphs of the original minerals which it has replaced, and that when such minerals had a fibrous structure, the secondary quartz formed therefrom is also fibrous.

The material examined in the present investigation was very kindly placed at our disposal by the Director of the Geological Survey of Mysore. It had been collected by Dr. Pichamuthu many years ago and the following description of the circumstances in which it had been found is quoted from his monograph[2] on the iron formations of the Eastern Bababudan Hills in Mysore.

"The writer has collected from various parts of the Bababudans specimens of fibrous quartz. In some of the siliceous layers which are formed of fibrous aggregates of quartz crystals, the fibres are disposed at right angles to the plane of bedding and are separable in some cases. The fibres are not always straight, but often bent. These layers frequently exhibit a chatoyant lustre. In micro-sections, these quartz layers are seen to contain fibrous amphiboles. Though in no one place it was possible to trace a layer of fibrous amphibole passing into a layer of quartz, the collections made by the writer show that the quartz has replaced amphibole. Similar fibrous quartz has long been known to occur associated with the banded ironstones of South Africa. The prevalent view in South Africa is that fibrous asbestos has been pseudomorphosed by silica."

2. Optical Behaviour

The material consisted of small rods each a few millimetres long and less than a millimetre thick. They were practically colourless. On the stage of the polarising microscope and immersed in a liquid of suitable index,

the material appears transparent. When the vibration direction of the polariser is parallel to the length of the specimen, the refractive index is nearly equal to the extraordinary index of quartz as judged by the Becke line test. Between crossed Nicols, the extinction is almost perfect when the longer dimension of the specimen is either parallel or perpendicular to their vibration directions. When a quartz wedge is introduced parallel to the length of the specimen, the interference colour rises in the Newtonian scale, thereby revealing that the *c*-axis of the quartz is parallel to the length of the specimen.

3. X-RAY EXAMINATION

The foregoing inference from the optical observations is generally confirmed by the results of the X-ray diffraction studies. Two typical examples of X-ray diffraction patterns taken with the specimens set *at right angles* to the direction of the X-ray beam are reproduced as Figs. 1 and 2 in Plate VI, Cu Kα radiation being employed. It will be recognised from the figures that the pattern is approximately a fibre diagram with the axis of the fibre nearly parallel to the *c*-axis of quartz which is set horizontal in the figures. There is however a certain lack of symmetry, indicating that the fibering is far from being as perfect as that shown by asbestos or by satin-spar. Figs. 3 and 4 are photographs taken with the same specimen as in Fig. 1 and with unfiltered Mo radiation, but with the specimen set *longitudinally* to the direction of the X-ray beam. The two figures represent slightly different settings of the rod. Had the quartz been truly fibrous, we should have expected to obtain a diagram consisting of complete circles. This is far from being actually the case and hence it would seem correct to describe the material as polycrystalline quartz with a preferred orientation for the *c*-axis rather than as truly fibrous quartz. Micro-sections of the original formation prepared by Dr. Pichamuthu and seen by us showed no break in continuity of the individual fibres along their length under the polarising microscope, thereby supporting the view of the structure indicated by the X-ray diagrams.

4. COMPARISON WITH CHALCEDONY

The principal reason why we have felt it desirable to place the results of the present study on record is in view of the earlier publications[3, 4] from this Institute on the structure of agate and chalcedony. Those studies had revealed that in the iridescent layers of banded agate, the crystallites of quartz are orientated predominantly along the *a*-axis, while in other regions the orientation is less specific. There were also indications of an alternative orientation for the fibre axis in chalcedony, namely the direction perpendicular to the first-order prism face of quartz. No case in which the fibering in chalcedony is parallel to the *c*-axis had been encountered by us. Had such

FIG. 1

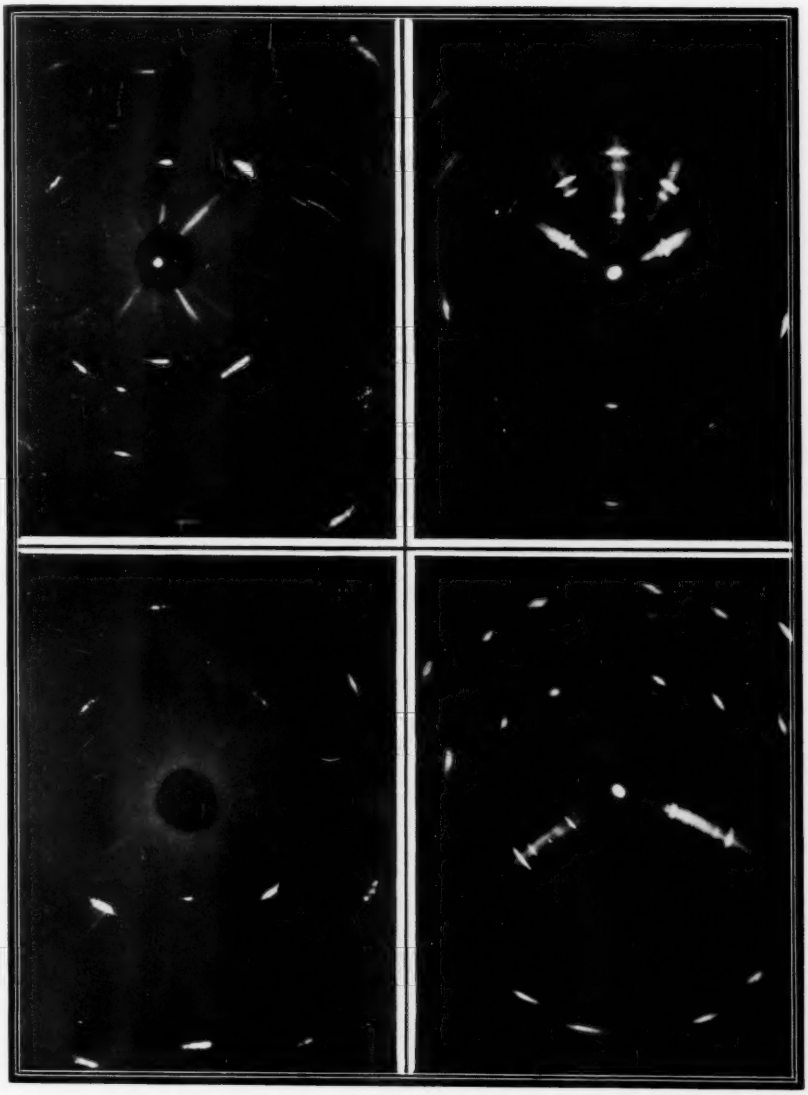

FIG. 3

FIG. 2

FIG. 4

a case been forthcoming, optical theory indicates that the material would have been transparent, almost resembling a single crystal of quartz in its behaviour.

5. Summary

The results of optical and X-ray examination of specimens of fibrous quartz from the Bababudan Hills in Mysore are described. They indicate that the material may be described as polycrystalline quartz with a strongly preferred orientation for the crystallographic *c*-axis along the length of the fibres.

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RAPID DETERMINATION OF URANIUM IN COMPLEX MINERALS LIKE SAMARSKITE, COLUMBITE-TANTALITE AND TITANONIOBATES

I. Volumetric Determination

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Received June 10, 1954

(Communicated by Dr. H. J. Bhabha)

During the course of analytical work in this laboratory need was felt for a simple, rapid and fairly reliable method of estimating uranium in complex minerals like samarskite. Due to the refractory nature of oxides of the earth acids the usual methods[1] employed for the decomposition of minerals of this class present many difficulties in getting all the material in solution. The earth acids hydrolyse in the presence of hydrochloric and nitric acids and consequently make it difficult to transfer all the material from the platinum dish as the hydrolysed product sticks hard to the metal. For the ideal separation of uranium either by carbonate,[2] cupferron,[3] extraction as uranous cupfferate,[4] ether extraction as uranyl nitrate[5] or by cellulose column[6] it is desirable that all the sample should be in complete solution. The complex minerals dealt with in this work, fail to give a clear solution of the sample. The only ideal solvent extraction of tantalum and niobium from uranium in an alloy has been devised by Harwell workers[7] from the fluorides using methyl ethyl ketone, the aqueous fraction containing the uranium.

In the new method outlined below the advantage is taken of the fact that these complex minerals usually break up with hydrofluoric acid and that uranium (VI) (uranium is invariably present both in quadrivalent and hexavalent states in these minerals) can be quantitatively reduced by stannous chloride and then precipitated as tetrafluoride along with the fluorides of thorium, rare earths and alkaline earths, which do not interfere in the subsequent estimation of uranium titrimetrically, after its reduction in the Jones Reductor.

Recommended Procedure

1. A convenient amount of the sample (5 g. if U_3O_8 is about 0·2%) is weighed into a platinum dish, moistened with water, 10 ml. of hydrofluoric acid (40%) are added and the dish heated on water-bath. If all the material is not decomposed 3–4 ml. of hydrochloric acid are added and the contents evaporated to dryness. 10 ml. of hydrofluoric acid are added and the contents again evaporated to dryness.

2. 10 ml. of hydrofluoric acid (40%) are then added and the solution stirred with a platinum rod. 2 g. stannous chloride are added to the solution. After diluting with distilled water to 50 ml. and digestion on water-bath for 15 minutes, the solution is allowed to stand overnight at room temperature.

3. The solution is filtered on a rubber or plastic funnel with Whatman No. 44, 9 cm. paper and washed twice by decantation with 1 : 4 hydrofluoric acid and finally transferred to the funnel and washed twice with hydrofluoric acid (1 : 4) and finally once with distilled water.

4. The precipitate is transferred back to the dish and the filter-paper charred in a platinum crucible and the ash added to the dish.

5. 2 ml. of concentrated nitric acid and 3 ml. of concentrated sulphuric acid are added to the dish and the contents heated cautiously on a sand-bath to vigorous fuming.

6. The dish is cooled and the contents diluted to 50 ml. with ice-cold distilled water and stirred until all the uranium is in solution.

7. The solution is passed through the Jones Reductor and washed twice with 2 N sulphuric acid and finally twice with distilled water and after aeration to oxidise trivalent uranium, is titrated with 0·05 N potassium permanganate standardised against standard uranium solution similarly treated in the Jones Reductor. A reagent blank is run through all steps of procedure. If cerium is present in the mineral ceric sulphate is used in the titration. From the ml. of permanganate or ceric sulphate used uranium present in the sample is calculated. Samples of samarskite, columbite-tantalite and titanoniobates were analysed by the above procedure for the uranium contents. In Table I are given the percentage U_3O_8 obtained by the usual (2nd column) and the present method (column 3).

Further work of estimation of trace amounts of uranium in these minerals by this method, is in progress.

TABLE I

Sl. No.	Nature of the mineral	Uranium oxide (U_3O_8%)		Remarks
		Values obtained by usual method	Values obtained by this method	
1	Columbite-Tantalite ..	20·54	20·62	containing (Cb_2+Ta_2) O_5=44·22% Thorium and rare earths
2	,, ,, ..	9·45	9·51	(Cb_2+Ta_2) O_5=44·24% ThO_2=1·57%, RE=11·17%
3	,, ,, ..	9·68	9·70	containing ThO_2 and rare earths
4	Samarskite	15·09	15·12	ThO_2=1·38% RE oxides=7·82%
5	,, ...	18·78	18·84	(Cb_2+Ta_2) O_5=45·36% ThO_2=1·76% RE oxides=9·54%
6	,, ...	14·26	14·32	ThO_2=1·64%, RE=9·21%
7	Columbite-Tantalite ..	8·18	8·20	(Cb_2+Ta_2) O_5=19·25% RE=10·60%, ThO_2=1·15%
8	,, ,, ..	7·56	7·70	(Cb_2+Ta_2) O_5=23% ThO_2=1·30 , RE=12·20%
9	Samarskite	10·11	10·13	(Cb_2+Ta_2) O_5=44% UO_2=1·76%, UO_3=8·44% ThO_2=3·56%, RE=15·73%
10	Yellowish brown powder	20·90	21·03	RE=8·38%, ThO_2=1·36%
11	Titanoniobate	0·89	0·93	(Cb_2+Ta_2) O_5= 31·2% TiO_2 = 31·3% ThO_2 = 0·15%

CONCLUSION

It will be seen from the above table that uranium in complex minerals can be determined fairly accurately within a period of one and half working

days. The method can also be applied to alloys of uranium. The principles of the method can also be applied to the estimation of uranium in any type of mineral. In the solution of the mineral, decomposed by usual methods, total R_2O_3 are precipitated by ammonium hydroxide, directly taken with hydrofluoric acid, reduced with stannous chloride and uranium determined by the procedure outlined above.

The author's sincere thanks are due to Dr. Jagdish Shankar for facilities and encouragement.

Summary

After breaking the samarskite and complex minerals with hydrofluoric acid, the hexavalent uranium in the sample is reduced to the tetravalent state by addition of excess stannous chloride. Uranium is thus precipitated as tetrafluoride along with the fluorides of thorium, rare earths and the alkaline earths, which do not interfere in subsequent titration of uranium after reduction in the Jones Reductor. The method is simple, rapid and uranium contents in samarskite columbite-tantalite and titanoniobate can be determined within the period of one and half working days.

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AN ABNORMAL τ-MESON DECAY

By R. R. Daniel and Yash Pal*
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Received September 2, 1954
(Communicated by Prof. B. Peters, F.A.SC.)

Abstract

An unusual example of a τ^+-meson decay in nuclear emulsions is described. From the measurements made on the momenta and direction of the three π-mesons emitted, the event is interpreted as a decay of a τ-meson according to the scheme:

$$\tau^+ \rightarrow \pi^+ + \pi^+ + \pi^- + \gamma + Q.$$

We have recently observed in a systematic investigation of the origin of slow π-mesons, an interesting example of a τ-meson brought to rest and decaying in an emulsion block detector flown for about three hours above an altitude of 70,000 ft., at Delhi, India.

Description of the Event

At first sight the event looked like an ordinary τ-meson decaying at rest. Among the decay products, two π^+-mesons could be identified by their decay and the third particle left the stack after traversing two more emulsions.

The Parent τ-Meson

From the characteristic increase of the coulomb scattering and grain density towards the end of its track, we conclude that the τ-meson had come to rest in the emulsion. (One must, however, bear in mind the possibility, though extremely unlikely, that the particle could have decayed before it was completely brought to rest, while it still had a small residual velocity.) The decay occurs 5·4 mm. from the processed edge of the emulsion. The τ-meson was followed through 90 emulsions 600 μ thick, equivalent to a total residual range of 8·70 cm., and found to originate from a star of the type $9 + {}^{1n}_{0p}$. The star is situated very near the glass emulsion surface. No other charged unstable particle was found among the nine black prongs all of which were brought to rest in the stack. The relativistic particle

* Now at the Massachusetts Institute of Technology, U.S.A.

connected with the star was followed through thirty-four emulsions (corresponding to a range of 2·14 cm.) to another star of the type $3 + 1\ p$. It is not possible to state which of the two is the parent star of the interconnecting particle.

Direct mass measurements on the τ-meson have been made, by the range-grain density method. The grain densities were estimated at intervals of about one centimetre, starting with a minimum residual range of 2·30 cm.; for each measurement about 500 grains were counted. All the plates in this stack have been developed very uniformly. The plateau grain density is $22 \cdot 5/100\,\mu$. In order to estimate the mass, we have made use of a range-grain density calibration obtained for another batch of emulsion with slightly higher plateau grain density, but similar grain size. Since our measurements are restricted to $g/g_{pl} < 2 \cdot 6$, corresponding to $R_\tau > 2 \cdot 0$ cm., this procedure is unlikely to lead to serious error. The mean mass value obtained from seven different measurements is $980 \pm 50\,m_e$, which is in good agreement with the ordinary τ-meson mass of $965\,m_e$.

The parent τ-particle is known to be positively charged, because two of the disintegration products have been identified as π^+-mesons. Its total time of flight is $0 \cdot 523 \times 10^{-9}$ secs.

The Disintegration Products

The τ-meson at the end of its range decays into three charged particles. Particles one and three are of low energy and are brought to rest in the same emulsion. Both of them undergo the characteristic π-μ-e decay, the μ-meson ranges being 578 and $599\,\mu$ respectively. The residual ranges of π_1^+ and π_3^+ are $3921\,\mu$ and $124\,\mu$, and their corresponding energies 13·60 and 1·85 MeV respectively.

Track number 2 is produced by a fast particle which leaves the stack after traversing two more emulsions. The track length in the first emulsion is 1·30 mm., and this region of the plate is sufficiently free from distortion to permit accurate scattering measurements. (Using the Bruxelles method we find in the relevant region of the first plate a maximum distortion of $K \simeq 80$ covans and in the direction of the track $K \simeq 10$ covans.) In the second and third emulsions the track enters a distorted region near the processed edge and its scattering there cannot be measured accurately. The application of the method of third differences to the scattering measurements made in the first plate showed that, if there was any distortion it was unimportant for the cell sizes employed (25, 50, 75 and $100\,\mu$). The final value of the $p\beta$ estimated from second difference is $p\beta = 56 \pm 9$ MeV/c.

A total of 469 grains was counted and the normalised grain density found to be equal to $1 \cdot 965 \pm 0 \cdot 09$. We have tested for possible abnormality in the grain density by making grain counts on one of the electrons from the π–μ–e decay belonging to the same event and to the same region of emulsion. The grain density was found to be normal. From these measurements the mass of this particle is estimated to be $315 \pm 75\ m_e$ which is consistent with the π-meson mass. Assuming it to be a π-meson, its energy calculated from the grain density is $30 \cdot 6 \pm 2 \cdot 2$ MeV.

INTERPRETATION OF THE EVENT

The kinetic energy of the three charged π-mesons adds up to $46 \cdot 1 \pm 2 \cdot 2$ MeV. This is far too small to be consistent with the well-known τ-meson Q-value of ~ 75 MeV. Further, measurements on the co-planarity of the three secondary particles showed, they are definitely not co-planar. Thus, it becomes necessary to interpret this event either in terms of new particles or in terms of a new decay scheme. If one wants to interpret the event in terms of known particles alone, the following possibilities must be considered.

(*a*) The event is not due to a τ-meson decay but to a capture star produced by a negative K-meson.

(*b*) The τ-meson decayed into three π-mesons before it was completely brought to rest.

(*c*) The event represents an alternative mode of decay of the τ-meson into three charged π-mesons and one or more neutral particles.

The first possibility seems extremely unlikely since no nuclear fragment or recoil is visible and since 95% of the rest mass of the K-meson appears in the form of π-mesons. Furthermore, the fragments show a net positive charge. As for (*b*), if the τ-meson had decayed in flight the combined kinetic energy of its decay products should be larger and not smaller than the Q-value of 75 MeV.

There remains the third alternative. Let us assume that one or more neutral particles are emitted together with the three charged π-mesons. Direct mass measurements on the τ-meson exclude the possibility, that the rest mass of the neutral particle (or the combined mass of the neutral particles, if there are more than one) could be as high as that of a μ-meson. Therefore, confining ourselves to known particles, we conclude that the rest mass of the neutral particle (or neutral particles) involved, is zero. The direction and magnitude of the momentum $\vec{p}_4$ carried away by the neutral decay

product(s) is obtained in Table I by adding vectorially the momenta of the three π-mesons.

TABLE I*

	x-component	*y*-component	*z*-component
p_1 (MeV/c)	62·5	0	7·1
p_2 (MeV/c)	−83·1±3·3	−39·6±1·6	−31·5±1·2
p_3 (MeV/c)	10·7	10·2	16·8
p_4 (MeV/c)	9·9±3·3	29·4±1·6	7·6±1·2
Vector sum	0	0	0

* The axis has been chosen along track 1, in the plane of the emulsion.

The absolute value of the momentum p_4 is equal to $32{\cdot}1 \pm 2{\cdot}7$ MeV/c. If we assume that the parent particle is the well-known τ-meson whose mass is known to be $965 \pm 2\, m_e$, we can now put an upper limit of $12\, m_e$ on the rest mass of the neutral decay product (or products). If we assume only *one* neutral particle of zero rest mass, then $E_4 = cp_4 = 32{\cdot}1$ MeV. In this case the Q-value is found to be $78{\cdot}2 \pm 4{\cdot}9$ MeV, which is in good agreement with the usual value. On the other hand, if we assume *more than one* neutral particle all of zero rest mass, then the Q-value will be larger than $78{\cdot}2 \pm 4{\cdot}9$ MeV, unless by accident the neutral particles are emitted in the same direction.

Thus, if this event is an alternative mode of decay of the known τ-meson, the fourth particle is most likely a γ-ray (a neutrino being ruled out because of its half integral spin). We, therefore, propose the scheme:

$$\tau^+ \rightarrow \pi^+ + \pi^+ + \pi^- + \gamma + Q$$

Knowing the direction of the γ-ray in space, we scanned the relevant emulsion volume up to a distance of 13·1 mm. (0·34 conversion units) for any associated electron pair. We did not find any.

So far in nuclear emulsions about 40 examples of the normal τ-decays: $\tau^{\pm} \rightarrow \pi^{\pm} + \pi^{\pm} + \pi^{\mp} + Q$ have been observed and only one event of the type mentioned above. Thus, this type of decay seems fairly rare. If one assumes that other unstable particles among whose decay products are charged π-mesons ($\wedge^{\circ}$, $\wedge^{\pm}$, θ°) will also occasionally emit a γ-ray, it may

explain a few abnormally low Q-values reported both in cloud chamber and in emulsion work.

ACKNOWLEDGEMENTS

We have pleasure in thanking Professor B. Peters for his continued interest and guidance.

We would like to express our thanks to Miss A. L. Damany who observed the event, and to D. Lal and Rama for helpful discussions.

DISTRIBUTION OF ELECTROLYTES ACROSS A SEMIPERMEABLE MEMBRANE IN THE PRESENCE OF ARSENIC TRISULPHIDE SOL

By A. K. M. Trivedi and M. J. Patani

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Received August 2, 1954

(Communicated by Dr. R. D. Desai, F.A.SC.)

There is a considerable divergence of opinion regarding the nature of the stabilizing electrolyte in the case of aged arsenic trisulphide sol.[1-4] It has been mostly assumed that hydrogen sulphide is the stabilizing electrolyte. On the other hand, Kargin and Klimovitzkaja[3] consider that in aged arsenic trisulphide sol, arsenious acid is the stabilizing electrolyte rather than hydrogen sulphide or thioarsenic acid. This is supported to some extent by Trivedi and Patani.[4]

When an electrolyte like sodium chloride is distributed across a semipermeable membrane (permeable to free electrolytes and water but practically impermeable to colloidal particles), the concentration of the reference substance (sodium chloride in this case), is affected adversely by (*a*) establishment of Donnan membrane equilibrium and (*b*) the volume occupied by the micelles, *i.e.*, the volume of the colloidal arsenic trisulphide *plus* water attached to it (which does not function as a solvent for the chloride). Establishment of the membrane equilibrium as well as the hydration of the micelles will increase the concentration of chloride per unit volume outside the membrane (Cl_E) as compared to the chloride concentration inside the membrane (Cl_I). On the other hand, if there is any adsorption of chloride by the micelles, it would tend to increase Cl_I as compared to Cl_E. The adsorption of chloride is ruled out as shown by Linder and Picton,[5] Whitney and Ober,[6] Kargin and Klimovitzkaja[7] and Trivedi and Patani.[8] Thus, the two factors responsible for the unequal distribution of chloride across the membrane are (*a*) and (*b*), which may be termed the membrane equilibrium effect and the hydration effect respectively.

Experimental

Concentrated arsenic trisulphite sols were prepared and analysed as before.[4, 8] At first, the aged arsenic trisulphide sol was suspended in the collodion bags[9] with water surrounding it. The volume of the liquid

available for analysis, however, was not found to be adequate to give sufficiently accurate results. The collodion bags were subsequently replaced by parchment paper bags. The parchment paper bags were found highly suitable for the purpose, both from the view-point of impermeability of colloidal particles as well as the volume of the liquid available for analysis. The bags could hold about 200 ml. of the liquid. Equilibrium was established in about twenty days. However, in all experiments, the bags

TABLE I

Estimation of Chloride, Arsenious Acid and Arsenic Trisulphide

Expt.	Wt. (gm.) arsenic trisulphide 10 ml. sol	Volume (ml.) for 100 ml. sol			Vol. (ml.) for 25 ml. sol N/20 Iodine solution
		N/10 Silver nitrate added	N/10 Potassium thiocyanate required for back titration	N/10 Sodium chloride†	
1 E	0·018	20·00	10·45	9·55	8·40
I	1·181	20·00	11·35	8·65	—*
2 E	0·012	20·00	10·95	9·05	9·00
I	1·154	20·00	11·80	8·20	—*
3 E	0·033	20·00	8·15	11·85	9·30
I	1·267	20·00	9·35	10·65	10·20
4 E	0·020	20·00	8·35	11·65	9·20
I	1·179	20·00	9·45	10·55	10·00
5 E	0·028	20·00	6·55	13·45	9·70
I	1·155	20·00	7·80	12·20	10·90
6 E	0·019	20·00	6·25	13·75	9·80
I	1·195	20·00	7·55	12·45	11·20
7 E	0·021	20·00	9·35	10·65	8·20
I	1·120	20·00	10·20	9·80	10·80
8 E	0·032	20·00	9·20	10·80	8·10
I	1·179	20·00	10·15	9·85	10·75
9 E	0·020	20·00	6·30	13·70	8·90
I	1·220	20·00	7·50	12·50	11·00
10 E	0·018	20·00	6·40	13·60	8·85
I	1·250	20·00	7·65	12·35	10·80

* *N.B.* Experiments could not be finished owing to an accident.

† Hydrochloric acid was used as a reference substance in experiment numbers 7, 8, 9, and 10.

were suspended uniformly for thirty days. The parchment paper bag was prepared by taking a parchment paper disc of 18 cm. diameter and folding it into a bag. The bag was tied to a rubber cork, through which passed a pyrex glass tube (1·0 cm. in diameter) closed on the top by means of another rubber cork. The apparatus was suspended in an outer vessel by means of another tight fitting cork 10 cm. in diameter and dipped in molten paraffin to remove any holes. The whole apparatus was made air-tight. These precautions are necessary to eliminate the evaporation of the liquid. The apparatus was kept in an air thermostat at $30 \pm 0{\cdot}5°$ C.

After equilibrium was attained, the liquid inside and outside the membrane was employed for various determinations, 100 ml. (taken with a 100 ml. pipette), 25 ml. and 10 ml. of the liquids being used for the determination of chloride, arsenious acid and colloid content respectively. In some cases, hydrochloric acid instead of sodium chloride was employed as a reference substance.

The results obtained are as in Table I above.

Discussion

Table II

Expt.	Concentration of arsenic trisulphide (gm./l.)		Concentration of chloride (m.e./l.)		Concentration of arsenious acid (m.e./l.)	
	I	E	I	E	I	E
1	118·1	1·800	8·65	9·55	..	16·8
2	115·4	1·200	8·20	9·05	..	18·0
3	126·7	3·300	10·65	11·85	20·4	18·6
4	117·9	2·000	10·55	11·65	20·0	18·4
5	115·5	2·800	12·20	13·45	21·8	19·4
6	119·5	1·900	12·45	13·75	22·4	19·6
7	112·0	2·100	9·80	10·65	21·6	16·4
8	117·9	3·200	9·85	10·80	21·5	16·2
9	122·0	2·000	12·50	13·70	22·0	17·8
10	125·0	1·800	12·35	13·60	21·6	17·7

Table II contains the concentrations of arsenic trisulphide in gm./litre and chloride and arsenious acid in terms of m.e./litre inside (I) and outside (E) the membrane. It will be seen that, in all cases, while the concentrations of chloride is greater outside (Cl_E) than inside (Cl_I) the bag, the reverse is the case with arsenious acid, *i.e.*, the concentration of total arsenious acid

is greater inside the bag than outside the bag. In the case of arsenic trisulphide, the concentration outside the bag is only 1 to 2% of the concentration inside the bag. If it is now assumed (this assumption will be justified later on) that, the ratio of free arsenious acid inside and outside the bag should be the same as the ratio of chloride inside and outside the bag, the concentration of free arsenious acid inside the bag may be calculated. This value, in all cases, is less than the concentration of arsenious acid inside the bag, as found experimentally. The difference between the two, therefore, will be the concentration of fixed arsenious acid. This is a definite proof of arsenious acid being adsorbed by colloidal particles. Since, a free electrolyte like sodium chloride or hydrochloric acid is not adsorbed, the adsorbed arsenious acid may, safely, be considered as the stabilizing electrolyte. The concentration of fixed arsenious acid in different experiments can be easily calculated. An example will make the procedure clear.

In Table II, Expt. III, the concentrations inside and outside the bag are 10·65 and 11·85 m.e./l. of chloride respectively and 20·4 and 18·6 m.e./l. of arsenious acid respectively. The concentration of free arsenious acid inside the bag will be $\frac{10 \cdot 65 \times 18 \cdot 6}{11 \cdot 85}$, *i.e.*, 16·74 m.e./l. Therefore, the amount of fixed arsenious acid will be $20 \cdot 40 - 16 \cdot 74 = 3 \cdot 66$ m.e./l.

Table III contains concentration of the stabilizing electrolyte per gm. of the colloid.

We may, now, consider in detail, the membrane equilibrium effect and the hydration effect. The presence of several diffusible ions will have a cumulative effect.[10] The concentration of total free electrolytes is about 30 to 40 m.e./l., while the concentration of fixed ion is about 3 to 6 m.e./l. Again, only a fraction of the latter may be responsible for influencing the equilibrium across the membrane.[11, 12] Thus, the concentration of fixed ions is only a fraction of the free electrolytes or ions present. Although the membrane effect is not itself reduced by the presence of free electrolytes, its relative importance, as a factor contributing towards the difference of free electrolytes across a membrane, relatively decreases as the concentration of free electrolytes is increased.[13] It can be easily shown that Cl_E–Cl_I will be independent of Cl_E in the case of membrane equilibrium effect; while in the case of hydration effect, Cl_E–Cl_I increases as Cl_E increases, being directly proportional to Cl_E.[14] If the various observations are arranged in order of Cl_E, it is easy to see that Cl_E–Cl_I increases as Cl_E

TABLE III

Determination of Fixed Arsenious Acid

Expt.	Concn. of arsenic trisulphide (I–E) (gm./litre)	Total arsenious acid present in 'I' (m.e./l.)	Free arsenious acid calculated for 'I' (m.e./l.)	Fixed arsenious acid (m.e./l.)	Arsenious acid per gm. of colloid. (m.e.)
1	116·3	..	15·22	..	..
2	114·2	..	16·32	..	..
3	123·4	20·40	16·71	3·69	0·02990
4	115·9	20·00	16·66	3·34	0·02881
5	112·7	21·80	17·60	4·20	0·03727
6	117·6	22·40	17·74	4·66	0·03962
7	109·9	21·60	15·09	6·51	0·05923
8	114·7	21·50	14·78	6·72	0·05860
9	120·0	20·00	16·24	3·76	0·03133
10	123·2	21·60	16·07	5·53	0·04488
				Mean ..	0·04059

increases. In the present case, therefore, Cl_E–Cl_I may be entirely attributed to the hydration effect. In that case, the ratio of the concentrations of arsenious acid and sodium chloride or hydrochloric acid will be the same, inside and outside the membrane.

Table IV contains the values of the apparent density of the particles (D) and specific hydrodynamic volume (S.H.V.), the density of amorphous arsenic trisulphide being taken as 3·1 gm./ml.[15] The average value of S.H.V. may be taken as 2·4. The extent of hydration may be calculated

TABLE IV

Expt.	Reference Substance	D	S.H.V.
1	Sodium chloride	1·234	2·512
2	,,	1·216	2·550
3	,,	1·219	2·544
4	,,	1·227	2·525
5	,,	1·213	2·558
6	,,	1·245	2·492
7	Hydrochloric acid	1·377	2·251
8	,,	1·304	2·378
9	,,	1·370	2·263
10	,,	1·342	2·313
	Mean ..	1·275	2·439

as before.[8] Thus, there are 25·1 $\left(\frac{1\cdot4}{18} \times \frac{1000}{3\cdot1}\right)$ millimoles of water to one gm. of arsenic trisulphide or there are 6·2 $\left(\frac{25\cdot1}{1000} \times 246\right)$ moles of water per mole of arsenic trisulphide in the micelles. The hydration found in the present case is greater than that reported previously[8]; wherein, the density of the coagulum was considered. This is natural as coagulation is partly a dehydrating process and again the membrane effect has been completely neglected in calculating the extent of hydration.

SUMMARY

In the case of aged arsenic trisulphide sol, arsenious acid is adsorbed on the colloidal particles and probably acts as a stabilizing electrolyte. The hydration in the case of aged arsenic trisulphide sol is found out by studying the distribution of electrolytes across a semipermeable membrane. The value of the hydration is 25·1 millimoles of water per gm. of the colloid. The hydration is greater in the sol conditions than in the coagulum.

ACKNOWLEDGMENT

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EFFECT OF TEMPERATURE ON ULTRASONIC VELOCITIES IN SOME INDIAN ROCKS

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1. Introduction

Studies in the laboratory, of velocities of sound in rocks, under high pressures and temperatures, facilitates a comparison with results obtained by direct seismological methods. Such investigations have been carried out by a number of workers and some interesting observations made. Ide (1937) using a dynamic method in the sonic range, studied the effect of temperature on elasticity for a number of rocks and glasses at ordinary pressures. His results indicate that no satisfactory measurements of elasticity can be made by heating rocks to 500° C. at ordinary pressures. At such temperatures, rocks begin to disintegrate as a result of anisotropic thermal expansion of crystals that compose the rock. He further pointed out that the velocity of sound decreases in most cases very markedly as the temperature rises and that it does not go back to its original value as the specimen cools. Birch and Bancroft (1940) working at 150° C. extended these studies to high pressures. Later, Birch (1943) determined the shear velocities alone for a number of igneous rocks upto 600° C. at high pressures. It is believed that the disintegration of rocks at such temperatures has been prevented to a large extent by the application of pressures of the order of 9,000 kg./cm.^{2} Hughes and Jones (1950) have determined the variation of elastic moduli for a number of igneous rocks with pressure and temperature employing the pulse technique. Hughes and Kelly (1952) studied the variation of dilatational wave velocities in sandstones and the effect of saturation with water on the same.

In an earlier paper, the author (1953) gave results regarding longitudinal and torsional velocities in a number of Indian rocks obtained by employing the ultrasonic pulse method. It is now thought desirable to study by this technique the effect of temperature on ultrasonic velocities in rocks under ordinary pressures, as it provides a dynamic method in the very high frequency region. Accordingly in the present paper are given the results regarding the variation of both longitudinal and torsional velocities in a few Indian rocks with temperature in the range of 3° to 110° C.

2. MAIN FEATURES OF EARLIER INVESTIGATIONS

Ide's work already referred to, deals with the effect of temperature on velocity of sound in glasses, metals and in rocks. He found that the velocity in some glasses increases with increasing temperature, the changes being perfectly reversible. Contrary to this, in the case of rocks, velocity decreases with increasing temperature. That only a part of the change in the velocity thus produced in reversible, and that the other part sets in permanently has also been noticed by Ide. This is a very significant result and the anisotropic expansion of crystals composing the rock which takes place when they are heated to 500° C. was held to be responsible for causing internal cracking along the lines of greatest stress. On cooling the specimen, the fractures remain, the crystals then becoming more loosely jointed. Irreversible changes that occur in most cases are presumably the consequences of such structural alterations. Ide noticed that in this respect, a dynamic method is superior to a static one because it may be expected to be less sensitive to the presence of fine cracks in a specimen. Pushing the same argument further, we may conclude that the application of a high frequency method, as is being done in the present investigation, is even more desirable if minute though extensive cracks are suspected. Hence a dynamic method is used in the present investigation, and the variation of both longitudinal and torsional velocities is studied over a temperature range of 3° to 110° C. In fact, the results obtained show that whatever changes occur in this range are such that they are perfectly reversible, *if sufficient time is given for the cooling of the rock specimen.* On the other hand, in conformity with the results of the earlier investigators, the position has been found to be quite different if the rock specimen is heated at ordinary pressures to higher temperatures such as 500 °C. It is noticed that large structural changes take place in the latter case and even the high frequency method employed here reveals these features.

3. EXPERIMENTAL TECHNIQUE

The experimental arrangement is the same as the one described earlier by Krishnamurthi and Balakrishna (1953). The liquid tank is immersed in a thermostatic bath and any desired temperature can be obtained and controlled within 1° upto 150° C. The lower temperature of 3° C. is attained by immersing the liquid tank in an ice-chest. The specimen is maintained at each temperature for about 30 minutes before readings are taken. The readings are taken at 3°, 28°, 80° and 110° C. Within the range of 3° to 80° C., water is used as a tank liquid. Meta-xylene (B.P., 138° C.) is chosen for the high temperature because of its low acoustic absorption.

In view of Ide's results and of conclusions drawn by Birch and his co-workers in this field, a control experiment has been first conducted and the results are given in Table I. All the velocities in this table are in metres/sec. and refer to room temperature (28 °C.).

TABLE I

	Unheated rock	Heated rock (110° C.)	
		Immediately after cooling	12 hours after cooling
Limestone I			
V_L	**6288**	6680	**6263**
V_T	**3211**	3246	**3225**
Heated a second time (Limestone I) ..			
V_L		6535	**6263**
V_T		3184	**3190**

It can be seen from the above table that within the range of 110° C., results are repeatable provided sufficient time is allowed for cooling. There is an apparent irreversibility and an abnormally high value is obtained, if the measurements are taken immediately after the surface alone of the rock cools but this abnormality disappears and the value settles down to the original one if sufficient time is allowed so that the whole interior is also cooled and conditions reach an equilibrium state. Another piece of limestone taken from the same rock as limestone I, showed a longitudinal and torsional velocities of 6396 and 3224 metres per second before heating. These results, as should be expected, agree with those obtained for limestone I. When this specimen was heated to 400° C. and cooled, its colour was found to have changed and a number of cracks were observed. It was not possible even to transmit the pulse through it. It is obvious that permanent changes of such a character have set in that the attenuation in the rock specimen is also considerably changed and the fact of our employing a very high frequency method does not help. Thus, contrary to Ide's results, it has been found in the present investigation that the results are repeatable in a given sample, if it is heated only upto 110° C., and allowed to cool. It may be safely concluded that the disintegration, if any, which sets in during this comparatively small temperature region is so fine that its effects are imperceptible if we employ a high frequency method for investigating the elastic properties.

4. RESULTS

V_L and V_T in Table II are longitudinal and torsional velocities respectively in meters/sec., as obtained in the present investigation.

TABLE II

No.	Name	3°		28°		80°		110°	
		V_L	V_T	V_L	V_T	V_L	V_T	V_L	V_T
1	Deccan trap ..	7353	2790	7270	2754	7008	2650	..	..
2	Nephelene Syenite ..	6181	2626	6044	2613	5720	2615	..	..
3	Limestone ..	6317	3104	6260	3065	6102	3009	6050	2970
4	Limestone ..	6317	3051	6237	3018	5938	2986	..	..
5	Shale	5736	2147	5620	2090	5282	1962	5128	1950
6	Gneiss	6828	3172	6739	3131	6621	3118	..	..
7	Charnokite ..	7792	3311	7575	3268	7203	3228	7069	3210
8	Charnokite ..	7208	3179	7123	3115	7008	3081	..	..

It is found difficult to determine these velocities for some of the rocks at 110° C. as seen from the above table, owing to high absorption in both the rock and the liquid used. Figure 1 shows the variation in each case, in a graphical manner. The numbers in the figure correspond to the serial numbers given in Table II for each rock.

5. DISCUSSION OF RESULTS

The variation of ultrasonic velocities, both longitudinal and torsional, with temperature is linear in the range of 3° to 110° C. in all cases studied, as can be seen from Fig. 1. The decrease of both the velocities markedly with increasing temperature in all cases as can be seen from Table II, is in accordance with the observations made by earlier workers. It may be noted that Ide has pointed out that the velocities decrease markdely in rocks, as temperature increases. The values of Ide in the case of limestone show that there is a change of about 300 metres per 100° C. change. This change is of the same order of magnitude as in the present investigation.

The temperature gradients for the two velocities in rocks calculated in the same manner as has been done by Birch (1943) are given in Table III.

It can be observed that in general the torsional temperature gradient is less than the longitudinal temperature gradient. The corresponding gradients in perspex, polystyrene, aluminium and NaCl respectively, are 2,000, 850, 450 and 839.* These gradients, it may be noted, are of the same order of magnitude as are obtained by the author for the rock specimens.

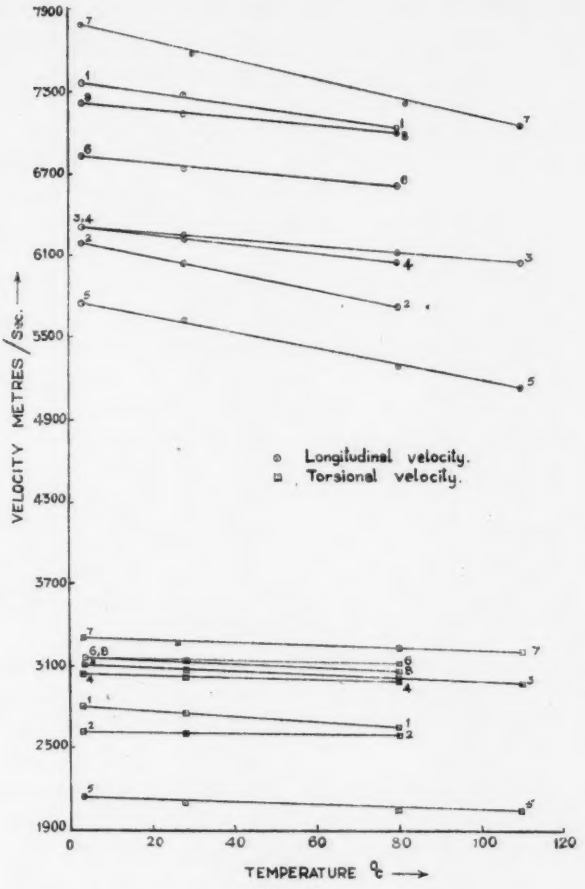

FIG. 1.

TABLE III

No.	Rock	$-10^6 \frac{1}{V_L} \cdot \frac{\Delta V_L}{\Delta T}$	$-10^6 \frac{1}{V_s} \cdot \frac{\Delta V_s}{\Delta T}$
1	Deccan trap	649	605
2	Nephelene Syenite	985	55
3	Limestone	395	395
4	Limestone	779	277
5	Shale	990	858
6	Gneiss	394	221
7	Charnokite	867	268
8	Charnokite	360	400

Birch and others working at high pressures, reported a smaller temperature gradient as shown in Table IV, than those observed in the present investigation, for all types of rocks.

TABLE IV

No.		$-10\frac{1}{V_s}\cdot\frac{\Delta V_s}{\Delta T}$	Pressure kg./cm.^{2}
1	Quartzite	25 20	3000 4000
2	Marble	129	3000
3	Diabase	105	3000
4	Dunite	167	8500
5	Granite	64	4000
6	Gabbro	108	5000

* These are calculated from the figures obtained by other workers in this laboratory. For Aluminium the values are taken from Bordoni and Nuovo (1953).

The low values shown in the above table are probably the result of the application of high pressures. In fact a small increase in the gradient as pressure decreases is noticed from the above table in the case of quartzite.

In the case of two limestones and two charnokites studied in the present investigation, there is a considerable difference in their temperature gradient as can be seen from Table III, though they have nearly identical compositions. A similar observation has been made by Birch in the case of two dunites which show variations of velocity with temperature differing by 30 per cent. and he has also observed that the velocity in Barre granite falls off at a rate which is scarcely half that found in Rock port and Chemsford granites. Even Ide's findings suggest discordant results for rocks of similar type.

6. SUMMARY AND CONCLUSION

The variations of both longitudinal and torsional velocities in the temperature range 3° to 110° C. have been determined in a few Indian rock specimens. It is observed that the variation is linear and the velocities

decrease markedly with increase of temperature. The velocities go back again to the original values as the specimens cool provided the maximum temperature at which the measurements are taken does not exceed 110° C. and the specimens are allowed to cool for a sufficiently long time. The temperature gradient of longitudinal velocities is generally higher than that of the torsional velocities. It is possible that the high frequency method employed in this investigation is such that it is insensitive to small structural changes, if any, that occur in the rock when it is heated at ordinary pressures to 110° C.

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THE ROLE OF SOLVENT IN CHEMICAL REACTIONS

Part I. The Reaction between Pyridine and Methyl Iodide *

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THE role of solvents on the course of chemical reactions is still far from clear, even though a good deal of work has been published. Menschutkin[13] classified solvents according as they accelerated or retarded a reaction and, from an analysis of rate constants, concluded that there was specific solvent solute interaction. Van't Hoff[19] analysed the effect into two parts: a catalytic one depending on the physical properties and another related to the solubility of the components, but his analysis of von Halban's work and of the Menschutkin reaction failed to give any conclusive results. Dimroth's refinement of the picture did not improve the situation but both Hawkins[7] and Lewis[12] noticed a rough correlation between the rate and the dielectric constant. Hinshelwood and his associates[8, 9] have made an extensive study of the reaction noticing distinct correlation between the two Arrhenius parameters. The work reported here deals with the reaction in 95 per cent. alcohol and in acetone.

EXPERIMENTAL

Pyridine, B.D.H. Analar, was dried over sticks of potassium hydroxide and distilled, large head and tail fractions being rejected b.p. 115° C./760 mm.

Methyl Iodide.—May and Baker L.R., was freed from elementary iodine by repeated washing with sodium carbonate solution, then washed with water, dried over anhydrous calcium chloride for several days in the dark and then fractionated in the dark, the middle fraction being collected, b.p. 42° C./760 mm.

Acetone was purified by the method of Norris and Prentiss,[17] the solvent being kept in contact with potassium permanganate with repeated shaking for several days (not less than 14 days were generally used), freed from precipitated manganese dioxide, and distilled. The distillate was dried over Merck's Extra Pure Anhydrous potassium carbonate for a week and then fractionated, b.p. 56° C./760 mm.

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* Based on the thesis of V.S.P. approved for the Ph.D. Degree of Madras University.

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Rectified spirit was fractionated twice, rejecting large head and tail fractions each time, fresh products being used each time. The solvent was found to be free from aldehydes, homologues and higher boiling fractions.

Benzene, crystallisable, for molecular weight determinations, was freshly distilled and used for extractions.

The reactions were carried out in an electrical thermostat, the thermal fluctuations being within 0·005° C. at 40° C., 0·01° at 50° C. and 0·02° at 60° C. Solutions of the amine and of methyl iodide were separately prepared and 5 ml. of each were mixed in a drawn-out 'Borosil' tube kept in a freezing mixture and then sealed off. The sealed tubes were then immersed in the thermostat, the time of immersion being taken as zero time (less than 1 minute was found to be needed for the tubes to reach the temperature of the thermostat and no great error was found to be introduced by this procedure). At suitable intervals, the tubes were taken out, cooled rapidly in

TABLE I

The Reaction in Acetone Solution

		Temperature °C.						
		40		50		60		
Strength of silver nitrate solution		0·02352 N		0·02496 N		0·02475 N		
Initial concentration of pyridine (a) gm. mol./l.		0·09727		0·09792		0·08459		
Initial concentration of methyl iodide (b) gm. mol./l. equivalent		0·08280		0·08549		0·07920		
Volume equivalent of amine in terms of silver nitrate (V_a)		41·35		39·22		34·18		
Volume equivalent of methyl iodide in terms of silver nitrate (V_b)		35·25		34·25		32·00		
		A		B		C		
A	Time (min.)	89·5	139·8	190·5	343·8	427·3		
	Volume (titre)	8·25	11·70	14·30	19·80	22·10		
B	Time (min.)	120·0	150·0	182·0	210·0	240·0	285·0	
	Volume (titre)	15·60	17·73	19·40	20·85	21·95	23·55	
C	Time (min.)	50·0	80·0	110·0	141·0	170·0	200·0	260·0
	Volume (titre)	10·60	14·15	16·95	18·85	20·20	21·70	23·45

TABLE II

The Reaction in 95 per cent. Ethyl Alcohol

		Temperature °C.						
		40		50		60		
Strength of silver nitrate solutions		0·02352 N		0·02504 N		0·02475 N		
(a) gm. mol./l. ..		0·09480		0·09893		0·09194		
(b) gm. mol./l. ..		0·08563		0·08539		0·07698		
V_a ml. ..		40·33		39·51		37·15		
V_b ml. ..		36·40		34·10		31·10		
		D		E		F		
D	Time (min.)	411·2	598·0	718·8	909·0	1282·0	1880·0	
	Volume (titre)	5·90	8·10	9·50	11·25	14·00	17·80	
E	Time (min.)	240·0	300·0	420·0	720·0	960·0	1200·0	1440·0
	Volume (titre)	7·85	9·40	11·83	16·25	19·30	21·38	23·00
F	Time (min.)	39·0	90·0	150·0	210·0	300·0	420·0	
	Volume (titre)	2·50	6·10	9·30	11·55	14·30	17·30	

freezing mixture, the tips broken off and the contents poured into a mixture of 30 ml. of ice-cold 2 N acetic acid and 30 ml. well-cooled benzene. The inside of the tubes were thoroughly washed out with ice-cold water. Five or six drops of eosin solution were added and the solution titrated rapidly against silver nitrate solution. The end-point was indicated by the aqueous layer turning pink through the adsorption of the indicator by the silver iodide solution. Benzene is used to help in keeping the unreacted amine and alkyl halide out of the aqueous layer. Acidimetric methods have been used for these estimations[1, 4] but we found that with pyridine, the end-points under the conditions of our experiment were not sharp and argentimetric methods gave more consistent results. The silver nitrate solutions were invariably standardised by gravimetric methods. Typical runs, in the two solvents used, are presented in Tables I and II above.

DISCUSSION OF RESULTS

The results presented here are for a completely homogeneous reaction and there was no separation of solid phase at any stage of the reaction.

They serve to some extent to supplement earlier observations of others.[9a, b, c] One difficulty in comparing earlier work should be mentioned here. The initial concentrations employed are such that separation of some of the product of the reaction should have taken place though the details provided give no indication on this point. Especially with non-polar solvents, homogeneous conditions may not prevail. Edwards[3] first drew attention to this aspect of the problem when he noticed that the dominant influence on the course of the reaction was the rate of crystallisation of the product. Davies and Cox[2] restricted their observations to the region up to which homogeneous conditions prevail. Neither of these, however, dealt with the pyridine-methyl iodide reaction. The rate constants and the Arrhenius parameters are convenient data for comparative studies and these are given in Table III.

TABLE III

Solvent	Rate Constant mol./l. sec.$^{-1}$ × 10^5.			E K. cals.	$Log_{10}PZ$
	40° C.	50° C.	60° C.		
Acetone ..	58·43	111·4	193·5	11·280	4·70
95% Alcohol ..	8·367	20·95	48·35	17·820	8·41

From the trend of the logarithm of the rate constant in relation to the dielectric constant of the solvent, it has generally been held that the reaction studied is one of the dipole-dipole type.[5, 14b] Kinetically, the alternatives are for a unimolecular and a bimolecular mechanism. The present studies, as well as the earlier published work, give consistently satisfactory second order rate constants over a considerable range of concentrations and ionisation of the alkyl halide may not be the rate-determining step. Essentially, the reaction is a three centre one, with simultaneous approach of the base and removal of the iodide ion. The driving force of the reaction is the availability of the unshared pair of electrons for co-ordination, while the inertia is provided by the polarisation of the C-I bond. The activation energy will involve the C-N and C-I bond energies and the repulsion energies of the reactants and products, while the entropy of activation or frequency factor arises from the need for the transition state in which the encounter between pyridine and the alkyl halide has to be in the region of the unshared electron pair and the alkyl group. All these factors are subject to environmental influence. However, since the products are ions, the coulombic attraction may more than offset the repulsion energy.

In analysing solvent influences, it will be convenient to take the data provided by other workers in other solvents and where these are not available, evaluating these parameters from the data provided. These are presented in Tables IV and V.

TABLE IV

The Pyridine-Methyl Iodide Reaction

Solvent	E K. cals.	$Log_{10}PZ$	Reference
60% alcohol-water ..	18·200	9·05	9(*b*)
95% alcohol-water ..	17·820	8·41	Present work
100% alcohol ..	18·000	8·32	9(*b*)
78·3% alcohol-benzene ..	17·200	7·86	do
47·5% do ..	15·900	6·99	do
15·5% do ..	14·900	6·28	do
100% benzene ..	14·400	5·55	do

TABLE V

Solvent	Reaction	E K. cals.	$Log_{10}PZ$	Reference
Ethyl alcohol ..	Pyridine-allyl bromide	15·100	10·9	7
100% alcohol ..	Pyridine-benzyl bromide	14·360	8·63	15
10% benzene alcohol ..	do	14·170	8·47	do
25% do ..	do	14·180	8·43	do
50% do ..	do	14·110	8·27	do
75% do ..	do	16·060	9·438	do
90% do ..	do	16·250	9·267	do
100% benzene ..	do	13·150	6·394	do
100% alcohol ..	Triethylamine-benzyl bromide	14·120	8·81	do
10% benzene alcohol ..	do	13·420	8·33	do
25% do ..	do	13·150	8·13	do
50% do ..	do	13·490	8·30	do
75% do ..	do	14·110	8·58	do
90% do ..	do	13·300	7·75	do
100% benzene ..	do	10·500	5·39	do
Alcohol ..	Dimethylaniline-benzyl bromide	13·200	8·78	10(*a*)

More work and a wider range of solvent compositions are needed before one can draw any conclusion in the case of alcohol-water mixtures. The activation energy, within the range studied, appears to be more or less constant but the frequency factor shows differences beyond the limits of experimental error.

The breakdown of any direct correlation between the Arrhenius parameters or the logarithm of the rate constant and dielectric constant is clearly

brought out by the results with benzene-alcohol mixtures. The figures in Table V have been obtained from the rate constant data reported by the Russian authors. In every one of the reactions, it will be noticed that benzene requires a lower activation energy than ethyl alcohol or mixtures of alcohol with benzene. Whether one considers the solvation of the complex in the transition state or the polarisation of the C-Hal. bond, a higher dielectric constant of the solvent may be expected to favour the process and lead to a corresponding reduction of the activation energy. The abnormal result can be partly accounted for in two ways. The Frank-Rabinowitch cage effect has been invoked by Norrish[16] in dealing with solvent influences. This involves a quasi-crystalline structure of liquids, demanding a fairly rigorous orientation of molecules and strong dipolar forces in solution. In mixed solvents, one may visualise the reactant molecules in an ordered (?) environment in which the solvent molecules of only one type are largely present and at a critical composition which may vary with temperature, a change similar to phase reversal in colloidal systems takes place. Further, if crystallisation takes place during the reaction, as seems likely in all the reported cases except in the present work and in alcoholic solutions of higher alcohol content, one has to reckon not only the rate of the reaction but also the rate of crystallisation and in computing true activation energies, one has to take into account the heat of crystallisation also. With such a picture, the macroscopic dielectric constant may differ considerably from the local value in the region of the reaction and a deviation from the $\log k - 1/D$ or $\log k - D\text{-}1/2D + 1$ relationship for a dipole-dipole reaction is only to be expected.

The need for considering a possible solvation of the transition state complex is also shown by the trend in E values in Table V with the different tertiary amines and the same alkyl halide in 100 per cent. alcohol. The low P values generally noticed for these reactions is also consistent with this picture that reaction is through the solvated reactant.

An analysis of all the results reveals one distinct feature. Both Arrhenius parameters are high in alcohol and the addition of alcohol or of water tends to increase both these. The difference noticed between acetone and alcohol is not peculiar to the reaction under investigation alone, as may be seen from the values of E for different reactions presented in Table VI.

Frequency factors also show a similar trend towards lower values in acetone. The reaction is, however, faster in acetone than in alcohol. indicating that the dominant factor affecting rate is the activation energy.

TABLE VI

Reaction	E in alcohol	Reference	E in acetone	Reference
Pyridine-methyl iodide ..	17·820	Present work	11·280	Present work
Pyridine-allyl bromide ..	15·100	7	13·490	10 *(b)*
Dimethyl aniline-benzyl bromide ..	13·200	10 *(a)*	9·747	10 *(a)*
Diethyl sulphide-methyl iodide ..	17·240	6	12·150	18

The abnormal features noticed can arise either through the ionisation of the base or the solvolysis of the alkyl halide. Even with isopropyl halides, Hughes[11] has shown that ether formation through S_N2 mechanism occurs to only 4 per cent. and in methyl halides may be expected to be less. As for hydrolysis, Moelwyn-Hughes has reported that the rate constant even at 100° C. is only $4{\cdot}47\times10^{-4,\,14a}$. Formation of pyridinium ion is possible in alcohol as well as in water and the addition of either of these to an organic solvent naturally leads to an increase in the formation of this reactant. This will tend to introduce the repulsion energy between the positive pyridinium ions and the positive pole of the alkyl halide. The net result is thus an increase in the activation energy. On the other hand the lowering of the activation energy in acetone can be traced to the strong attractive forces between the polarised alkyl halide and the carbonyl group of the solvent.

SUMMARY

The reaction between pyridine and methyl iodide has been studied in 95 per cent. ethyl alcohol and in acetone. The reaction is faster in the latter solvent at the three temperatures studied. The Arrhenius parameters have been evaluated and the variations discussed in relation to solvent influences.

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ELLIPTIC POLARISATION OF LIGHT SCATTERED BY COLLOIDAL SOLUTIONS

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1. Introduction

It is well known that the important conclusions derived from Mie's theory (1908) of light-scattering by large spherical particles are the finite depolarisation of the transversely scattered radiation when the incident light is unpolarised, the dissymmetry of the angular distribution of scattering and the ellipticity of the transversely scattered radiation when the exciting radiation is plane polarised in an arbitrary azimuth. Of these the last, namely the ellipticity, has been shown on theoretical grounds to be a sure test of the multipolar character of the scattering of light by any isotropic symmetric medium (Perrin, 1939, 1942). Nevertheless, experimental studies on the elliptic polarisation of light scattered by colloidal media are few. Using the Babinet Compensator method suggested by Sir C. V. Raman (1941) the light scattered by certain heterogeneous media was shown to be elliptically polarised by Darbara Singh (1942), Hariharan (1942), R. S. Krishnan and Venkata Rao (1944), and A. George (1950). Conclusions of a qualitative nature were drawn by them regarding the size of the scattering particles from the range of angles of polarisation of the incident light over which they were able to observe any ellipticity in the transversely scattered light. As will be shown later in the paper, their experimental approach to the problem of the elliptic polarisation of the scattered light was such as not to bring out clearly the implications of Mie's theory. The present investigation has therefore been undertaken in order to examine in greater detail the theoretical conclusions concerning the phase difference and the amplitudes of the vertical and the horizontal components of the scattered radiation when the azimuth of polarisation of the incident radiation is varied. Suitable experimental methods have been used to analyse the scattered radiation in some emulsions and sulphur sols containing particles which are known to be spherically symmetric and of uniform size.

2. Theoretical Considerations

According to Mie's theory, if the incident beam of light is polarised with vibrations vertical or horizontal, the light scattered in the transverse

horizontal direction will be completely polarised. In the former case, the electric vector of the scattered light will be perpendicular to the plane of scattering, while in the latter it will be in the plane of scattering. The corresponding intensities are given by equations (1) and (2).

$$J_{\perp} = K \left| \sum_{1}^{\infty}{}_{\nu} - (A_{\nu}\pi_{\nu} - P_{\nu}\pi_{\nu}') \right|^2 = K \left| (a + ib) \right|^2 \quad (1)$$

$$J_{\parallel} = K \left| \sum_{1}^{\infty} (A_{\nu}\pi_{\nu}' - P_{\nu}\pi_{\nu}) \right|^2 = K \left| (c + id) \right|^2 \quad (2)$$

where K is a constant equal to $\lambda^2/4\pi^2r^2$, r being the distance of the observer from the centre of the particle. π_{ν} is an easily calculable function of the angle of scattering γ, and π_{ν}' is its derivative. A_{ν} and P_{ν} are complicated functions of $2\pi R/\lambda$ and m, where R is the radius of the spherical particle, λ the wavelength of light and m the relative refractive index of the particle. Several numerical computations of A_{ν} and P_{ν} for particles of different sizes and relative refractive index exist in the literature which render quantitative comparison with theory possible. [Blumer (1925, 1926), Lowan (1948), R. O. Gumprecht and C. M. Sliepcevich (1951, 1952), Bernice Goldberg (1953), Kerker and Perlee (1953), Gucker and Cohn (1953) and Boll, Gumprecht and Sliepcevich (1954)].

In formulæ (1) and (2) the quantities within brackets are complex quantities whose absolute values are to be taken for evaluating the intensities of scattering. But the amplitudes of vibration corresponding to $J_{\perp}$ and $J_{\parallel}$ which may be put in the form $a + ib$ [see equations (1) and (2)] have in general a certain difference of phase with respect to the components of the incident electric vectors which give rise to them, the phase of these vibrations being with respect to the centre of the spherical particle.

Let us now suppose that the particle is illuminated by a beam of light polarised at an angle α to the vertical. The incident electric vector of unit intensity may be resolved into two components $\sin\alpha$, in the plane of observation and $\cos\alpha$ perpendicular to it. These components of the incident vibration are in phase. In the transverse horizontal direction the intensities of the perpendicular and parallel components of the scattered radiation are given by

$$J_{\perp} = K \mid (a + ib) \mid^2 \cos^2\alpha \quad (3)$$

$$J_{\parallel} = K \mid (c + id) \mid^2 \sin^2\alpha \quad (4)$$

These two components combine to form an elliptically polarised radiation and the phase difference δ between the vertical and horizontal components

is then given by

$$\delta = \tan^{-1} b/a - \tan^{-1} d/c \qquad (5)$$

δ may however be positive or negative depending on the size and refractive index of the scattering particles (Kastler, 1952). It is to be pointed out that δ the phase difference is independent of the angle of polarisation α and depends only on the size and relative refractive index of the scattering particle and the angle of scattering γ. Thus as α is varied from 0 to 90°, one observes in the transverse horizontal direction a continuous variation of the ellipticity, namely the ratio of the minor to the major axis of the ellipse, which increases first from 0 to a finite value depending on ρ_u and then decreases to zero again, the *phase difference between the vertical and the horizontal components remaining however constant.* It follows from Mie's theory that this phase difference is a characteristic quantity of the scattering element like intensity of scattering and depolarisation.

If the observation is not restricted to the transverse horizontal direction alone, as the phase difference fluctuates with the angle of scattering (Van de Hulst, 1947), for certain angles of observation depending on the size and relative refractive index, the incident linearly polarised light can give rise to circularly polarised light. A complete study of the elliptic polarisation of the scattered light should therefore include a measurement of the phase difference δ, and a determination of its sign, a determination of the orientation of the axes of the ellipse with respect to the horizontal and vertical, the ellipticity or the ratio of the axes and its variation with the angle of polarisation of the incident beam.

If the direction of incidence be along OZ of a rectangular co-ordinate system, and the observation along OY, then the elliptic vibration representing the scattered radiation, when the plane of polarisation of the incident light is inclined at an angle α to the vertical (OX) has for its components

$$z = p_1 \sin \alpha \sin \omega t$$

$$x = p_2 \cos \alpha \sin (\omega t + \delta) \qquad (6)$$

where $p_1 \sin \alpha$ and $p_2 \cos \alpha$ are the complex amplitudes, δ the phase difference and ω the circular frequency. Then θ the inclination of the axis of the ellipse to the horizontal is given by (Theory of Optics—Schuster and Nicholson, 1924).

$$\tan 2\theta = \frac{\sqrt{\rho_u} \sin 2\alpha}{(1+\rho_u)\sin^2 \alpha - 1} \cos \delta \qquad (7)$$

since $\rho_u = (p_1)^2/(p_2)^2$. From this it is seen that there exists a relation between the orientation of the ellipse, the phase difference between the vertical and the horizontal components, the depolarisation factor ρ_u and the angle of polarisation α. Thus as stated earlier, if the scattering medium consists of large spherically symmetric particles of uniform size, δ is the same and is a constant and the result of varying α would be to produce elliptically polarised radiation of different orientations and axial ratios. It follows from equation (7) that for a value of α given by $\cot^{-1}\sqrt{\rho_u}$, θ the inclination of the axis of the ellipse is 45° and the corresponding value of ρ_α is 100%.

If one analyses the scattered light using a Babinet Compensator set with its axes vertical and horizontal, then as the plane of polarisation of the incident beam is rotated, the fringes due to the elliptically polarised scattered radiation will not show a continuous shift with respect to the crosswire. On the other hand, if the compensator is set with its axes at 45° to the vertical as was done by the earlier workers [Darbara Singh (1942), Hariharan (1942), R. S. Krishnan and Venkata Rao (1944) and A. George (1950)] the fringes as seen through the Compensator will shift continuously with reference to the crosswire in spite of the fact that δ is a constant. The phase difference $(\phi_2 - \phi_1)$ with respect to the axes of the Compensator, which was the quantity measured by the earlier workers is given by

$$\tan(\phi_2 - \phi_1) = \frac{\sqrt{\rho_u}\sin 2\alpha}{1 - (1 + \rho_u)\sin^2\alpha}\sin\delta. \qquad (8)$$

It is also possible to evaluate δ from the above equation using the measured values of ρ_u, α and the corresponding $(\phi_2 - \phi_1)$. But this is not the direct method of measurement of δ, which is a characteristic parameter of the scattering particle.

3. Experimental Details

To carry out visual observations a strong source of light was necessary. Consequently in all the measurements to be described below, sunlight reflected by means of a Foucault single mirror Heliostat was used as the source of illumination. The light was condensed by means of a Dallmeyer photographic lens of focal length 12″ fixed to cover an aperture in the wall of a darkened room. By using a small aperture a nearly parallel beam was obtained and this was allowed to fall on the colloid contained in an optical glass cell, suitable precautions being taken to avoid errors due to stray light, etc. Since the orientation of the elliptic vibration had to be determined it was necessary to rotate the Babinet Compensator about the direction of the scattered radiation and know accurately the orientation of the principal

axes of the Compensator. This was achieved by the use of a Fuess polarising microscope kept with its axis horizontal in conjunction with a Fuess Babinet Compensator analyser combination. The orientation of the principal axes could be accurately read off from the graduated circle of the microscope. A green filter was placed in the path of the incident beam to obtain a narrow band of wavelengths of high intensity. This was essential for accurate measurements since the fringes are well defined only for monochromatic or nearly monochromatic radiations. A cell containing alum solution was used to cut off the heat radiations in the incident light. A large square ended nicol was used to polarise the incident beam and the angle of polarisation could be read off on a graduated circle.

A direct measurement of δ was also made by using the Babinet Compensator with its axes vertical and horizontal. For any arbitrary angle of polarisation, if there exists a measurable difference of phase between the vertical and the horizontal components of the scattered light the crosswire would no longer be at the centre of a dark or bright band but would have shifted to some other position depending on δ. The shift which gives the phase difference will be constant when the angle of polarisation is varied; only the visibility of the fringes will undergo a change. The sign of the phase difference as well as the other characteristics of the elliptically polarised radiation may easily be determined with the help of a quarter wave plate and a nicol. As such observations on the sign of δ, etc., were made using also a $\lambda/4$ plate and an analyser mounted on graduated circles, by methods which may be found in any standard treatise on optics.

4. Preparation of Emulsions and Sols

Two different emulsions were prepared for the study, namely (1) Bergamont oil in water, (2) Lemon oil in water. The uniformity of the droplets and the stability of the emulsion depend on the mode of preparation. Consequently to obtain stable emulsions the following method was adopted.

About 400 c.c. of pure double-distilled water was rendered dust-free by slow distillation for a third time after carefully filtering the water through a fritted glass funnel which also contained a pad of Seitz bacterial filter. To this water was added a solution of 1 c.c. of the oil in 5 c.c. of alcohol and then the whole thing was refluxed for about 36 hours in a ground glass apparatus. During this process the alcohol was completely removed and the initial thick emulsion was broken up into one containing more finely divided oil droplets. The emulsion was then filtered through a pyrex glass porous filter in order to homogenise the emulsion. The emulsions were

then examined under a high power microscope having an eyepiece with a micrometer scale and the size of the droplets estimated.

The preparation of sulphur sols by a wide variety of methods is well known. However, it was only recently that strictly monodisperse stable sols of sulphur containing spherical particles were prepared by La Mer and Co-workers (1946 *et seq.*) and their optical properties studied in detail. Since such sols are ideal for measurements, the results of which are to be compared with those of Mie's theory, three different sulphur sols were prepared for the present work using the method of La Mer and Barnes (1946). Initially two solutions, one of A. R. sodium thiosulphate and the other A. R. sulphuric acid were prepared, the strength of each solution being 1·5 N. To 995 c.c. of pure dust-free distilled water kept in a litre resistance glass volumetric flask, 1 c.c. of the 1·5 N acid solution was added. The flask with its contents was then thermostated at 26° C. To this dilute acid solution 1 c.c. of the 1·5 N thiosulphate solution was added rapidly and the volume made up at once to a litre. The solution was mixed thoroughly and returned to the thermostat. Portions of the solution were examined optically at different time intervals. The sulphur particles were found to grow at a uniform rate, at any instant the sol being strictly monodisperse. The appearance of well-defined Tyndall spectra as the particles continued to grow was used as a criterion of monodispersivity. The number of spectral orders and their position vary with the particle radius. All the phenomena of this nature recorded by La Mer and Barnes were reproduced in the sols prepared for the present study and it was therefore concluded that these sols were also strictly monodisperse and contained spherical particles. In order to preserve the stability of the sols during the period of measurement the sols obtained by removal of aliquot portions from the litre flask at different time intervals were titrated with very dilute iodine solution until about 70% of the free thiosulphate was neutralised.

Upto a radius of $\cdot 2\mu$ the depolarisation factor for a sulphur sol is a monotonic function of size. The radius of the particles in sol A which contained the smallest particles was found to be in this range and hence the radius of the particle was determined by measuring the depolarisation factor ρ_u for incident unpolarised green light, using the well-known Cornu method. From the value of ρ_u the particle radius was found to be about $\cdot 184\mu$. For the other two sols B and C, which were obtained by allowing the particles to grow further, this method of size determination could not be used since ρ_u is no longer a monotonic function of the size but fluctuates violently beyond the size limit of about $\cdot 2\mu$. Hence the radius was determined from observations on a number of orders of Tyndall spectra. Sol B

gave four well-defined red orders and the particle radius was estimated to be between $\cdot 31\,\mu$–$\cdot 34\,\mu$. Sol C gave five red orders and so the radius was taken to be between $\cdot 33\,\mu$–$\cdot 39\,\mu$ (Barnes *et al.* 1947).

5. Results and Discussion

The experimental results of the measurements on the elliptic polarisation of the scattered light are given in Tables I and II and Fig. 1. In the tables for each sol the experimental values of ϕ defining the orientation of the elliptic vibration for different angles of polarisation α are given in the second column. In the next column are given the values of δ calculated from equation 7 using the experimentally measured value of ρ_u. Finally in each case the average value of the phase difference δ determined by using the Compensator with its axes vertical and horizontal has also been given.

In Fig. 1 the experimentally measured values of $(\phi_2 - \phi_1)$ in the case of emulsions have been plotted against the angle $(90 - \alpha)$ (circles and squares)

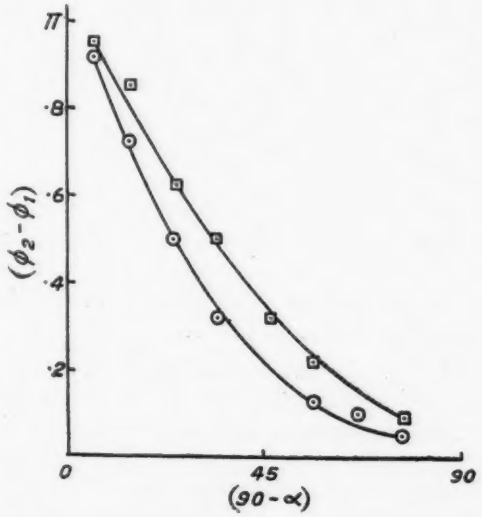

Fig. 1. Variation of $(\phi_2 - \phi_1)$ with $(90-\alpha)$ where α is the angle of polarisation.

and the smooth curves represent the theoretical relation between $(\phi_2 - \phi_1)$ and $(90 - \alpha)$ according to equation 8. The agreement between the two is found to be quite satisfactory. From the curves the angles α at which $(\phi_2 - \phi_1) = \pi/2$ found to be $66 \cdot 5°$ and $58°$ for lemon oil and Bergamont

oil emulsions respectively, compare well with the values 67° and 57° obtained for α when $\theta = 45°$.

From Table I it can be seen that for emulsions, δ is sensibly constant irrespective of the angle of polarisation. The orientation θ of the elliptic vibration, however, changes as one rotates the polarising nicol from the vertical towards the horizontal. Furthermore it is seen that for both emulsions there is a very good agreement between the calculated values of δ and the average measured value of δ. Although the refractive index relative to water is small in both cases ($\sim 1 \cdot 15$) the large phase difference may be attributed to the large size of the particles in both the cases. It can also be seen that the angle α at which the orientation of the ellipse is 45° is such that $\cot^2 \alpha$ is nearly equal to ρ_u, the actual values of $\cot^2 \alpha$ being ·42 and ·18 for Bergamont oil and lemon oil emulsions respectively while the values of ρ_u are ·4 and ·19.

Coming next to the case of sulphur sols the behaviour is found to be quite similar to that of the emulsions. In the case of sol A which contains particles of the smallest size the constant phase difference is also the least and is negative. It is found that for sulphur sol A the value of $2\pi R/\lambda$ corresponding to the measured value of δ (Kastler, *loc. cit.*) leads to a particle radius R equal to $\cdot 19\,\mu$. This agrees well with the value of $\cdot 18\,\mu$ obtained from a measurement of the depolarisation factor ρ_u for incident unpolarised light, the mean wavelength of the incident radiation being taken as 5,400 Å.U. In the case of sols B and C which contained particles of large size, δ is also numerically larger but remains negative. No comparison could, however, be made with the theoretical values of δ calculated from Mie's theory as the values of A_ν, P_ν for such large particles were not available. In the case of sulphur sols also it is seen that the value of α at which $\theta = 45°$ is such that $\cot^2 \alpha$ is equal to the value of ρ_u measured directly. Thus for sol A $\cot^2 \alpha = 1 \cdot 15$ is identical with the measured value, while for sols B and C the measured values of namely 1·34 and 2·04 are also practically the same as the values of $\cot^2 \alpha$ *viz.*, 1·32 and 2·04.

It is clear from what has been said above that a complete study of the scattering of light by any colloidal medium should therefore include measurements of intensity, polarisation of the scattered light and also the phase relationship between the vertical and the horizontal components for incident linearly polarised light. In the present investigation we have restricted ourselves to the case of large spherical particles. An experimental study of the scattering of the light by large anisotropic particles with special reference to the ellipticity is in progress.

TABLE I

Emulsions

Bergamont oil emulsion			Lemon oil emulsion		
$\alpha°$	θ	$\delta°$	$\alpha°$	θ	$\delta°$
16	7	−48	16	5	−46
26	12·5	−47	26	8·6	−46
36	18·5	−49	36	13	−46
46	29	−46	46	19	−46·3
57	45	..	56	29	−43·5
66	59	−48	67	45	..
76	73·5	−46	76	66	−49

Bergamont oil emulsion.—Average measured value of $\delta = -50°$; $\rho_u = 0·4$.
Lemon oil emulsion.—Average measured value of $\delta = -48°$; $\rho_u = ·19$.

TABLE II

Sulphur Sols

Sol A			Sol B			Sol C		
$\alpha°$	θ	$\delta°$	$\alpha°$	θ	$\delta°$	$\alpha°$	θ	$\delta°$
16	14·5	−35·3	16	14·7	−42	16	14·5	−55·5
26	25	−34	28	28	−41·7	28	31	−58·4
36	36·5	−34·5	41	45	...	35	45	..
43	45	..	56	65·5	−41	56	73	−56·3
56	60	−33·2	76	80·75	−42·3	76	84·5	−57·3
66	70	−33·3	..	..	..	..	..	..
76	79	−34·7	..	..	..		..	..

Sol A.—$\rho_u = 1·15$; Average measured value of $\delta = -32°$.
Sol B.—$\rho_u = 1·342$; Average measured value of $\delta = -40·5°$.
Sol C.—$\rho_u = 2·04$; Average measured value of $\delta = -55°$,

Summary

By an analysis of the theoretical conclusions of Mie's theory concerning the elliptic polarisation of the scattered light when the incident light is plane polarised in an arbitrary azimuth, the significance of the phase difference between the vertical and the horizontal components has been pointed out. It has been shown how the experimental investigations so far carried out have failed to bring out clearly the implications of Mie's theory. Using suitable experimental methods to analyse the scattered radiation in some emulsions and monodisperse sulphur sols containing particles which were spherically symmetric and of uniform size, the constancy of the phase difference has been established by three different methods of measurement. The value of the phase difference calculated from the available Mie scattering functions for one sulphur sol agreed well with the measured value and the characteristics of the transversely scattered elliptically polarised light for different azimuths of polarisation of the plane polarised incident light, were in accordance with the predictions of Mie's theory.

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ERRATA

ELASTIC CONSTANTS OF ORTHORHOMBIC SULPHUR

By R. V. G. Sundara Rao

In a paper published in these *Proceedings* (Rao, 1950), the author had reported the results of measurements of the determination of the elastic constants of orthorhombic sulphur.

Due to oversight, in converting the elastic constants C_{ij} into the compliances s_{ij}, a systematic mistake crept into the latter.

The following are the correct values of s_{ij} corresponding to the C_{ij} given on page 275 in the above article:—

$s_{11} = 70 \cdot 9$	$s_{22} = 83 \cdot 4$	$s_{44} = 232$
$s_{12} = -35 \cdot 6$	$s_{23} = -14 \cdot 9$	$s_{55} = 115$
$s_{13} = -13 \cdot 4$	$s_{33} = 30 \cdot 3$	$s_{66} = 132$

$$\beta = 56 \cdot 8 \times 10^{-13} \text{ cm.}^2 \text{ dyne}^{-1}$$

The above are in units of cm.^{2}/dyne.

The error was pointed out by Dr. W. A. Wooster to whom the author's thanks are due.

References

Sundara Rao, R. V. G. .. *Proc. Ind. Acad. Sci.*, Sec. A, 1950, **32**, 275.

Vol. XL, Section A, No. 2, August 1954

In the graph on page 103 the portions corresponding to 0 to 50 days may be ignored.

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Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

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